

⑨



Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number:

0 335 575
A2

C49

⑫

EUROPEAN PATENT APPLICATION

⑮ Application number: 89302842.3

⑮ Int. Cl. 4: D21D 3/00

⑯ Date of filing: 22.03.89

⑰ Priority: 28.03.88 GB 8807444
27.06.88 GB 8815219

⑲ Date of publication of application:
04.10.89 Bulletin 89/40

⑳ Designated Contracting States:
AT BE CH DE ES FR GB IT LI NL SE

⑴ Applicant: ALLIED COLLOIDS LIMITED
P.O. Box 38 Low Moor
Bradford West Yorkshire, BD12 0JZ(GB)

⑵ Inventor: Langley, John Graham
4 Wharfedale Gardens
Bailldon Shipley West Yorkshire BD17
6TM(GB)

⑶ Representative: Lawrence, Peter Robin
Broughton et al
GILL JENNINGS & EVERY 53-64 Chancery
Lane
London WC2A 1HN(GB)

⑸ Production of paper and paper board.

⑸ Paper or paper board is made by providing an aqueous cellulosic suspension containing a cationic polymer and then adding cationic starch or a high molecular weight synthetic cationic polymer, subjecting the suspension to shear, and then adding inorganic material selected from bentonite or colloidal silica. The process is of particular value when the suspension is formed from a mechanically derived pulp and/or deinked pulp and when the product is to be newsprint or board.

EP 0 335 575 A2

Production of Paper and Paper Board

Paper or paper board is made by providing a thick stock, diluting the thick stock to form a thin stock, draining the thin stock to form a sheet and drying the sheet. The thick stock can be made either by mixing water into dried pulp or, in an integrated mill, by diluting a drained pulp.

It is standard practice to improve the process performance, or the product quality, by including various additives at one or more of these stages.

For instance, if the pulp from the which the thick stock is made is impure, the normal way of preparing it for drainage is by adding inorganic material, such as alum, talc or bentonite, at the pulping or thick stock stages. These treatments can have the effect of minimising problems due to pitch and other sticky materials.

If it is necessary to improve the strength of the final sheet it is common to include a dry strength resin, for instance a cationic starch, in the stock that is to be drained.

It is standard practice to include cationic polymers in the stock that is to be drained in order to improve drainage and/or retention.

Processes for improving retention are described in U.S. 4,388,150 and involve the addition of cationic starch and colloidal silicic acid to the stock before drainage. Such processes have been commercialised under the trade name "Composil" (trade mark).

Processes that give improved drainage, retention, drying and formation are described in EP 235893 and involve adding a first synthetic cationic polymer before a shear stage and bentonite after that shear stage. Such processes have been commercialised under the trade name "Hydrocol" (trade mark).

Although this process gives very good results in most instances, there is room for improvement with some stocks, especially impure stocks, and for some end products, for instance newsprint and board.

In the invention, paper or paper board is made by a process comprising providing a cellulosic suspension, subjecting this to one or more shear stages selected from cleaning, mixing and pumping stages, adding a main polymer, selected from substantially linear synthetic cationic polymer having molecular weight above 500,000 and cationic starch, before one of the shear stages and adding inorganic material selected from bentonite and colloidal silicic acid after that shear stage, draining the suspension to form a sheet and drying the sheet, and in this process there is a preliminary polymer inclusion stage selected from (a) the inclusion in the suspension before the main polymer of a low molecular weight water soluble synthetic cationic polymer having molecular weight lower than the molecular weight of the main polymer, and (b) the inclusion of a water soluble synthetic cationic polymer as a drainage aid for the drainage of cellulosic pulp when the suspension is made by draining a cellulosic pulp (in the presence of the drainage aid) and diluting the drained pulp.

The preferred aspect of the invention comprises the incorporation of the said low molecular weight water soluble synthetic cationic polymer.

The inclusion of the low molecular weight cationic polymer in the thin stock before addition of the main polymer can lead to improvement in the processing and performance properties obtained by the addition of the main polymer before a shear stage and bentonite or colloidal silicic acid after that shear stage. For instance, depending upon the other conditions, it can lead to reduced problems due to pitch and other sticky materials and can lead to improved wet and/or dry strengths, runability, drainage, linting, opacity and other paper qualities.

In this first aspect of the invention, the aqueous cellulosic suspension can be made either from dried pulp or, in an integrated mill, by diluting a drained pulp, all in conventional manner.

In the second aspect of the invention, the cellulosic suspension is made by diluting a drained pulp in an integrated mill and the drainage of the pulp is promoted by including a pulp drainage aid in the pulp that is to be drained, this draining aid comprising a water soluble cationic polymer. The cationic polymer for this purpose can be any of the synthetic polymers discussed below for use as the main cationic polymer.

When draining a pulp, in an integrated mill, to form a wet pulp that can then be diluted to make the thick stock and the thin stock, it is common to include no drainage aid in the pulp since drainage often occurs adequately without incurring the expense of a drainage aid. However in this aspect of the invention it is desirable to include a drainage aid since it promotes drainage and/or retention and provides a drained pulp that already contains cationic polymer and the inclusion of this cationic polymer has beneficial effects on the subsequent treatment with the described main polymer and the inorganic additive. For instance it can reduce the amount of main polymer that is required for optimum performance and the combined amount of drainage aid and main polymer may then be approximately the same as the optimum amount of main polymer if the pulp had not been treated with drainage aid. Thus by applying drainage aid the process

can be improved both at the pulp drainage stage and the sheet formation stage but the total amount of polymer that is used is substantially unchanged and the final performance quality can be substantially unchanged.

The amount of drainage aid polymer is usually at least 0.005 or 0.01%, often at least 0.03 or 0.05%, but it is generally unnecessary for it to be more than 0.3% or, at the most, 0.5%. Amounts of 0.1 to 0.2% are often preferred. These percentages are based on the dry weight of the pulp.

The synthetic polymeric drainage aid can be a drainage-promoting, relatively low molecular weight polymer, for instance any of those discussed below as the polymer having lower molecular weight than the main polymer, but is generally a relatively high molecular weight polymer for instance having a molecular weight conventional for dewatering aids and retention aids. For instance the polymer typically is a substantially linear synthetic cationic polymer having molecular weight above 500,000, and preferably having intrinsic viscosity above 4dl/g. Thus it may be any of the polymers described in EP 0235893.

Intrinsic viscosities herein are derived in standard manner from determination of solution viscosities by suspended level viscometer of solutions at 25 °C in 1 Molar NaCl buffered to pH about 7 using sodium phosphate.

Irrespective of whether or not the thick stock is made by dilution of a wet pulp that has been drained in the presence of a drainage aid, it is preferred in the invention to incorporate the described low molecular weight soluble synthetic cationic polymer before the main polymer.

It is preferred that the remainder of the process should be similar to the "Hydrocol" process and, thus, should be otherwise conducted as in EP 235893, using a synthetic cationic polymer having molecular weight at least 500,000 before one of the shear stages and bentonite after. The materials and processing conditions described in EP 235893 can be used in the invention, subject to the modification that the suspension includes the low molecular weight polymer before addition of the main polymer. Alternatively, and less preferably, the bentonite can be replaced by colloidal silicic acid or other suitable fine particulate material or the synthetic polymer can be replaced by cationic starch.

Sometimes lower amounts of the main polymer than are recommended in EP235893 can give good results in the present invention, for instance amounts of less than 300g/t e.g. 50g/t (0.005%) to 250g/t, especially above 100g/t based on the dry weight of the stock.

The process can alternatively be similar to that described in US4388150 with the addition of cationic starch into the suspension prior to the colloidal silicic acid (which can be modified as WO86/5826).

The low molecular weight polymer can be present in the thick stock that is diluted to form the thin stock or it may be added to the thin stock. For instance generally the thick stock is diluted to form the thin stock by use of white water. It is desirable to add the low molecular weight polymer before, or immediately after or during, the dilution with white water and to add the main polymer to the thin stock, after the addition of the low molecular weight polymer.

The low molecular weight polymer should have a molecular weight sufficiently lower than the molecular weight of the main polymer that it will provide different process or performance benefits. For instance this aspect of the invention does not include a process in which both the low molecular weight and high molecular weight polymers are primarily cationic retention aids. Instead, it is restricted to processes in which the low molecular weight polymer does provide a different performance benefit. Generally the low molecular weight polymer has intrinsic viscosity below 2dl/g and usually has molecular weight below 500,000. The molecular weight is usually above 50,000 and often above 100,000.

A preferred relatively low molecular weight polymer is polyethylene imine. A suitable grade of this type of polymer is the material sold under the trade name Polymin SK. Other suitable materials are polymers and copolymers of diallyl dimethyl ammonium chloride, of dialkyl amino alkyl (meth) acrylates and of dialkylaminoalkyl (meth) acrylamides (both generally as acid addition or quaternary ammonium salts), as well as polyamines and polydicyandiamides-formaldehyde polymers. Amphoteric synthetic polymers may be used.

One preferred process according to the invention utilises a relatively crude stock containing significant amounts of pitch and/or having high cationic demand. For instance it may require at least 0.1% Polymin SK to give improved retention when the Polymin SK is used in conventional manner as retention aid. Polymin is a trade mark. Such stocks are, for instance, those containing more than 25% by weight, usually more than 50% by weight, of mechanically derived pulps and/or deinked pulps. By mechanically derived pulps we mean groundwood, pressure refined groundwood, thermo-mechanical, chemi-thermo mechanical or any other high yield mechanically derived fibres.

In these instances, the low molecular weight polymer can be selected primarily to reduce cationic demand and/or avoid pitch problems and/or linting.

When using these relatively crude pulps, the process is of particular value when the stock is to be used

for the manufacture of newsprint, and for this purpose stock is generally substantially unfilled or only contains small amounts of filler, for instance 0 to 15% and often 0 to 10% based on the dry weight of the stock. Benefits are however also achieved if the stock contains filler in amounts to give up to 30% filler in the final paper produced.

The process is also of value in the manufacture of board, again often from similar crude pulps containing little or no filler. In these instances an alternative or additional property of the low molecular weight polymer may be to improve the strength of the board and for this purpose a low molecular weight water soluble synthetic cationic dry strength resin may be used as the polymer. Amphoteric polymers are particularly suitable for this purpose.

The amount of low molecular weight polymer is up to 0.5% generally in the range 0.01 or 0.05 to 0.2%, based on the dry weight of the stock, and the optimum can be found by routine experimentation. Often the pulp, before treatment with the low molecular weight polymer, has a cationic demand (as measured by titration with the main cationic polymer) of above 400g/t and the low molecular weight polymer is included in the stock, or ahead of the stock, in an amount to reduce the cationic demand of the thin stock to below 300g/t before adding the main polymer.

The process of the invention is found to give an improvement in the performance since it can give improved pitch and/or stickies removal, improved paper quality such as opacity and linting characteristics improved wet strength or runnability during manufacture. Furthermore the performance of the process when assessed in terms of the drainage characteristics is improved by the incorporation of the second polymer, as compared to a process without that polymer, for instance a process as described in EP235893 or US4388150.

In the following examples, Polymer A is a polymer of IV 7dl/g formed from 75% acrylamide and 25% dimethylaminoethyl acrylate, MeCl quaternised, and Polymer B is a modified polyethyleneimine as sold under the trade name Polymin SK.

Example 1

A 100% mixed waste stock having a consistency of 0.5% was prepared. Drainage tests were conducted on the stock using a modified Shopper Riegler freeness tester, the time for 600mls of backwater to drain from the stock sample being measured. The stock was subjected to shear and the drainage was measured. In one test no additions were made before or after the shear. In other tests bentonite was added after the shear and polymer A and/or polymer B was added before the shear. When both polymers A and B were added, B was added considerably ahead of polymer A.

The results are as follows.

Table 1

Polymer B	Polymer A	Bentonite	Drainage
0	0	0	74
0	0.04%	0.2%	32
0.02%	0.04%	0.2%	18
0.04%	0.04%	0.2%	13
0.04%	0	0.2%	51

Example 2

A process similar to the preceding example was conducted using a stock having a high mechanical fibre content, and in particular being a 50:50 groundwood:bleached kraft pulp having a consistency of 1.0%. In addition to measuring the drainage time as in the previous example, a pitch count was made (in particles/ml by the Allen method). The following results were obtained.

Table 2

Polymer B	Polymer A	Bentonite	Drainage	Pitch Count	Percentage Pitch Reduction
0	0	0	80	5.8×10^6	
0	0.025%	0.2%	49	1.7×10^6	70%
0.025%	0.025%	0.2%	35	1.2×10^6	79%
0.05%	0.025%	0.2%	31	5.1×10^6	91%

These examples clearly demonstrate the value of adding, for instance 0.01 to 0.1%, generally around 0.02 to 0.07%, polyethylene imine so as to reduce the amount of high molecular weight (for instance IV above 4) cationic retention aid that is required for good drainage and retention and so as to counteract the effect of stock having high cationic demand and, especially, high pitch count.

Example 3

Newsprint is made using a stock based on 3% kraft, 17% magnesite, 38% thermomechanical pulp and 42% groundwood, and to which 20% broke has been added. High molecular weight polymer is added, in some tests, just before the last shear stage and bentonite is added, in some tests, after the last shear stage. Low molecular weight polymer is added to the thin stock soon after it is diluted from the thick stock.

In these tests the low molecular weight polymer is polymer K which is a solution polymer of about IV 1 dl/g and formed from about 20% acrylamide and 80% by weight diallyl dimethyl ammonium chloride. The high molecular weight polymers are L, which is 70% acrylamide, 30% methyl chloride quaternised dimethylaminoethyl acrylate IV 8, and polymer M which is 95% acrylamide and 5% methyl chloride quaternised dimethylaminoethyl acrylate IV 11. The drainage rate for each of the treated suspensions is measured, with the best results being those that have the highest drainage figure. The results are as follows.

Table 3

Polymer K	High MW Polymer	Bentonite	Drainage
0	0	0	205
0.2%	0	0	195
0.2%	0	0.2%	300
0.2%	0.05%L	0.2%	335
0.2%	0.05%M	0.2%	340
0	0.05%M	0.2%	325

These results clearly demonstrate the benefit in the manufacture of newsprint from adding high molecular weight cationic polymer immediately before shear and bentonite after shear even when the high molecular weight polymer only has a relatively low cationic charge, and they also show that a useful result can be obtained when the high molecular weight polymer is replaced by a lower molecular weight polymer having molecular weight above 500,000, but that best results are obtained using a combination of both.

Claims

1. A process in which paper or paper board is made by forming an aqueous cellulosic suspension, passing the suspension through one or more shear stages selected from cleaning, mixing and pumping stages, adding a main polymer selected from cationic starch and high molecular weight water soluble cationic polymer to the suspension before one of the shear stages and adding inorganic material selected from bentonite and colloidal silica after that shear stage, draining the suspension to form a sheet and drying

the sheet, characterised in that the process includes a preliminary polymer inclusion stage selected from (a) adding to the suspension, before the addition of the main polymer, a low molecular weight water soluble synthetic cationic polymer having molecular weight lower than the molecular weight of the main polymer and (b) adding a water soluble, cationic, polymeric, drainage aid to a cellulosic pulp and then draining the pulp and diluting the drained pulp to form the aqueous cellulosic suspension.

2. A process according to claim 1 in which the main polymer is a high molecular weight linear water soluble cationic polymer having molecular weight above 500,000.

3. A process according to claim 2 in which the inorganic material is bentonite.

4. A process according to any preceding claim in which at least 25% by weight of the cellulosic suspension is formed from mechanically derived pulp and/or deinked pulp.

5. A process according to any preceding claim in which the product is newsprint or board.

6. A process according to any preceding claim in which the main polymer is a synthetic polymer having intrinsic viscosity at least 4dl/g or is cationic starch and a low molecular weight water soluble synthetic cationic polymer having lower molecular weight is incorporated in the suspension before the main polymer.

7. A process according to claim 6 in which the low molecular weight polymer has intrinsic viscosity below 2dl/g.

8. A process according to claim 6 in which the low molecular weight polymer has molecular weight 100,000 to 500,000.

9. A process according to any of claims 6 to 8 in which the low molecular weight polymer is selected from polyethylene imine, polyamines, polycyandiamide formaldehyde polymers, amphoteric polymers, and polymers of monomers selected from diallyl dimethyl ammonium chloride, diallylaminoalkyl (meth) acrylates and dialkylaminoalkyl (meth) acrylamides.

10. A process according to any of claims 6 to 9 in which the low molecular weight polymer is an amphoteric cationic dry strength resin and the product is board.

11. A process according to any of claims 6 to 10 in which the suspension to which the low molecular weight polymer is added has a cationic demand, as measured on the main cationic polymer, of at least 400g/t and the amount of low molecular weight polymer that is added reduces the said cationic demand to below 300g/t.

12. A process according to any of claims 6 to 11 in which the suspension that is drained to form the paper or paper board is a thin stock formed by dilution of a thick stock and the main polymer is added to the thin stock and the low molecular weight polymer is present in the thick stock.

13. A process according to claim 12 in which the suspension that is drained to form the paper or paper board is a thin stock formed by dilution of a thick stock and the main polymer is added to the thin stock and the low molecular weight polymer is added to the thin stock or to the thick stock in an amount of from 0.01 to 0.5% based on the dry weight of suspension.

14. A process according to any preceding claim in which the suspension that is drained to form the paper or paper board is made by diluting a drained pulp that has been made by draining a cellulosic pulp containing a pulp drainage aid and in which the drainage aid comprises a water soluble, cationic, synthetic, polymeric drainage aid having intrinsic viscosity above 4dl/g.